

Instrumental Methods

The following section describes representative commercial instruments for determining total C in soils. They were chosen to illustrate the principles involved in instrumenting total C analysis. The inclusion of the following three instruments does not imply that they are superior or inferior to others currently being marketed. As with all instruments, various evaluation procedures should be used to determine and to confirm the validity of data obtained in comparison to accepted, standard methods. Tabatabai and Bremner (1991) described automated instruments available for determining total C in soils as well as which instruments are capable of simultaneous determination of N or S.

Carbo-Erba NA 1500. Carlo-Erba Instruments (Milan, Italy) developed an automated instrument capable of simultaneous determination of C, H, and N in geologic materials, soils, and other environmental samples. The principles involved, development of the instrument and a description of modes of operation are presented by Pella (1990a,b). A sample is placed in a tin sample cup, crimped to confine it, and introduced into a quartz reactor. For mineral soils, a typical sample size is 5- to 10 mg, necessitating the use of samples finely ground in a ball mill or similar apparatus. The quartz reactor is maintained at 1050°C with a constant flow of He. Flash combustion will occur if a pulse of O₂ is injected into the quartz reactor shortly after introduction of the sample. Under these temperature and O₂ conditions, the tin is oxidized to SnO₂ resulting in the temperature increasing to 1700 to 1800°C and the complete combustion of soil organic matter. The combustion products (CO₂, N oxides, and H₂O) are swept by the helium carrier gas through chromium dioxide (CrO₂) to catalyze oxidation of organic fragments and CO₂O₄ coated with Ag to remove halogens and sulfur oxides. The gases then flow through a heated Cu (650°C) column to remove excess oxygen, Mg(ClO₄)₂ to remove H₂O and into a chromatographic column for separation of N₂ and CO₂. The different gases are detected with a thermal conductivity detector. A generalized flow diagram for this instrument is shown in Fig. 34-2.

Schepers et al. (1989) evaluated the NA 1500 coupled with a mass spectrometer for simultaneous determination of C, N, and ¹⁵N in soil and plant materials. The NA 1500 yielded N and ¹⁵N data comparable to that obtained with conventional manual methods (Kjeldahl digestion followed by mass spectroscopy analysis). A detailed comparison of C data was not conducted although realistic values for total C in soils and plant materials were obtained. An evaluation of sample preparation methods (soil grinding/Wiley mill vs. ball milling) indicated that homogeneous soil and plant samples were essential to reduce analytical variability, especially in view of the typical sample size of 10 mg. Verardo et al. (1990) have described procedures for using the NA 1500 to determine C and N in marine sediments. Due to the analysis of 5 to 10 mg, careful sample preparation and grinding are needed to insure that a representative sample is analyzed. As with any analytical method, the inclusion of appropriate standards and blanks is essential to insure valid total C data. The capability of coupling this instrument with a mass spectrometer is a potential benefit as well.

Leco Instruments. The LECO Corporation (St. Joseph, MI) has marketed instruments for automated analysis of total C in soils and other solid materials for the past several decades.

A description of Leco instruments is presented by Tabatabai and Bremner (1991). Earlier results with the Leco automatic 70-s C analyzer (Tabatabai &

Bremner, 1970; Carr, 1973) indicate that reliable soil total C data are obtained using Fe, Sn, and tin-coated copper accelerators in an induction furnace followed by thermal conductivity to quantitate CO₂. The newer LECO IR-12 instrument involves combustion of a soil sample in an induction furnace using an O₂ atmosphere followed by passing the gas mixture over a catalyst to convert CO to CO₂ and CO₂ quantitation with an infrared detector. A related instrument, model DC-12 Duo-Carb, involves combustion of samples mixed with V₂O₅ (vanadium pentoxide) in an induction furnace heated to 1000°C under an O₂ atmosphere. The CO₂ produced is measured with a thermal conductivity detector.

In 1993, LECO marketed two instruments for determining total C in soils. Both instruments utilize resistance furnaces to combust samples at >950°C. In the Model CR-412, a sample contained in a ceramic boat is placed in a specially designed horizontal resistance furnace maintained at a constant temperature in the range of 950 to 1400°C under O₂ flow. After a delay, O₂ is directed onto the sample and carries the CO₂ released through dust and water vapor traps and into an infrared detection system. Merry and Spouncer (1988) evaluated the earlier model CR-12 and found that it gave reasonable soil organic C values when operated at 1200°C. In an evaluation of combustion temperature on C recovery from noncalcareous and calcareous soils, it was found that both inorganic and organic C were recovered between 600°C and 1000°C. Total C determined by the CR-12 and the Allison method (Allison, 1960; see "Wet Combustion Method") were in close agreement for 20 Iowa soils (Yeomans & Bremner, 1991).

Chichester and Chaison (1992) evaluated the CR-12 for determining organic C and inorganic C by combusting samples at 575°C and 1000°C, respectively. They recommended combustion at 575°C for 250 to 360 s to determine organic C followed by combustion at 1000°C for 250 s to determine inorganic C. In addition, the time required for analysis of inorganic C could be reduced from 250 to 60 s by increasing the combustion temperature from 1000°C to 1371°C. In summary, total C could be determined by a single combustion at 1371°C as found by other investigators.

A second LECO instrument is the model CHN 600 which is capable of simultaneous analysis of C, H, and N. A flow diagram for the CHN 600 is shown in Fig. 34-3. The successor to the CHN 600 is the model CHN 1000. A soil sample (<200 mg) is placed in a tin capsule and combusted in a resistance furnace at 950°C using O₂ as a carrier gas. The gases formed are scrubbed to remove S gases and equilibrated in a ballast chamber. After equilibration, the gas mixture flows through two infrared detectors set to detect CO₂ and H₂O. An aliquot of the gas mixture is analyzed for N₂ by thermal conductivity after reduction of N oxides and removal of CO₂ and H₂O.

The CHN 600 has been used in several soils studies. Total C results from 20 Iowa soils were essentially the same using the CHN 600 and a standard wet combustion method (Yeomans & Bremner, 1991). A comparison of data obtained by the CHN 600 with a LECO induction furnace instrument and a wet-oxidation method indicated that the CHN 600 was the most precise total C technique (0.01-0.12% C) and enabled a technician to perform 90 to 100 analyses in an 8-h d (Sheldrick, 1986). The CHN 600 has been shown to recover 100% of the C in a range of pure organic C compounds (acetanilide (N-acetylaniline), sucrose (C₁₂H₂₂O₁₁), sulfanilic acid (C₆H₇NO₃S), and EDTA (C₁₀H₁₆N₂O₇)) and, as expected, to yield soil organic C values 16 to 59% greater than those obtained by the Walkley-Black method (McGeehan & Naylor, 1988). In general, the CHN 600 has shown to be a reliable and accurate instrument for the determination of total C in soils.

Perkin-Elmer CHN2400. The Perkin-Elmer (Perkin-Elmer Corp., Instrument

Division, Norwalk, CT) simultaneously measures C, H, and N using the principles employed in the traditional Pregl and Dumas procedures. A sample contained in a platinum boat is oxidized with O_2 at $-1000^\circ C$ for 2 min in a combustion tube in the absence of carrier gas (He) flow. After combustion, He flow is initiated and the CO_2 , H_2O , and N_2 bases produced by combustion are passed over CuO to convert CO to CO_2 and silver mesh (silver vanadate or silver wool) to remove S and halogen gases. The gases then flow into a tube maintained at $650^\circ C$ and packed with copper granules between end plugs of silver wool, where quantitative reduction of N oxides to N_2 occurs. The gases are brought to constant pressure and volume in a gas mixing chamber and then allowed to expand into the analyzer portion of the instrument. The analyzer consists of three thermal conductivity (TC) detectors connected in series and separated by two traps. The sequence of TC detectors and traps enabling quantification of H, C. and N is as follows:

1. TC detector 1 (output equals total gas composition).
2. Magnesium perchlorate trap to remove H_2O .
3. TC detector 2 (decrease in output from detector 1 is proportional to H content).
4. Soda asbestos plus $Mg(ClO_4)_2$ trap to remove CO_2 .